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Technical Report No. 18

Molecular Structure of Graphite/Polyimide Interphases

by

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Prepared for Publication

in

Composite Interfaces

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JUN 0.9 1992
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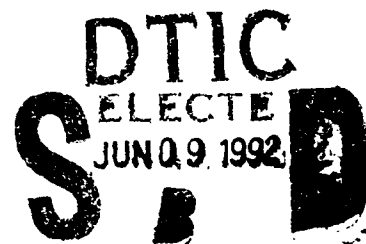
May 22, 1992

92-14883

92 6 05 010

REPORT DOCUMENTATION PAGE

REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
None	None

SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
None	This document has been approved for public release and sale; its distribution is unlimited.
DECLASSIFICATION / DOWNGRADING SCHEDULE	
None	

PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Technical Report #18	

NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
University of Cincinnati		Office of Naval Research

ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Department of Materials Science Cincinnati, Ohio 45221-0012	800 North Quincy Street Arlington, VA 22217

NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Office of Naval Research		N00014-89-J-1590

ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
800 North Quincy Street Arlington, VA 22217	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
	N00014-89	J-1590	413m012	

1. TITLE (Include Security Classification)

Molecular Structure of Graphite/Polyimide Interphases

2. PERSONAL AUTHOR(S)
W. H. Tsai, J. T. Young, and F. J. Boerio

3a. TYPE OF REPORT	13b. TIME COVERED FROM ___ TO ___	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical Report		May 22, 1992	39

5. SUPPLEMENTARY NOTATION

7.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

9. ABSTRACT (Continue on reverse if necessary and identify by block number)

The molecular orientation of adsorbed polyimides and model compounds with respect to highly oriented pyrolytic graphite (HOPG) surfaces was determined by reflection-absorption infrared (RAIR) spectroscopy. As the thickness of pyromellitic diimide (PMDI) films decreased, bands near 766 and 729 cm^{-1}, which were assigned to the CNC out-of-plane bending modes, were relatively strong in the spectra, demonstrating that PMDI was adsorbed flat-down with the imide rings parallel to the HOPG surface. As the thickness of N,N'-diphenylpyromellitic diimide (DPPMDI) films was decreased, bands near 1785 and 1722 cm^{-1}, which were assigned to the C=O stretching modes, were relatively strong in the RAIR spectra. Moreover, bands near 869, 841, 742, and 686 cm^{-1} attributed to the out-of-plane bending modes of monosubstituted benzene rings became considerably stronger. It was suggested that the DPPMDI molecules nearest to the HOPG surface were

3. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION	
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified	
a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Dr. Joann Milliken	(202)696-4410	

19. Abstract (continued)

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December 31, 1991

ABSTRACT

The molecular orientation of adsorbed polyimides and model compounds with respect to highly oriented pyrolytic graphite (HOPG) surfaces was determined by reflection-absorption infrared (RAIR) spectroscopy. As the thickness of pyromellitic diimide (PMDI) films decreased, bands near 766 and 729 cm^{-1}, which were assigned to the CNC out-of-plane bending modes, were relatively strong in the spectra, demonstrating that PMDI was adsorbed flat-down with the imide rings parallel to the HOPG surface. As the thickness of N,N'-diphenylpyromellitic diimide (DPPMDI) films was decreased, bands near 1785 and 1722 cm^{-1}, which were assigned to the C=O stretching modes, were relatively strong in the RAIR spectra. Moreover, bands near 869, 841, 742, and 686 cm^{-1} attributed to the out-of-plane bending modes of monosubstituted benzene rings became considerably stronger. It was suggested that the DPPMDI molecules nearest to the HOPG surface were adsorbed edge-on with the carbonyl groups perpendicular to the surface and with the monosubstituted benzene rings parallel to the surface. There were significant differences in relative band intensity observed between the transmission and RAIR spectra of polyimides derived from pyromellitic dianhydride (PMDA) and oxydianiline (ODA). The band near 1725 cm^{-1} due to the C=O stretching mode increased its relative intensity in the RAIR spectra of PMDA/ODA polyimides while the bands near 1499 and 1237 cm^{-1} due to the ODA moieties decreased their relative

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I. Introduction

Interfaces between polymer matrices and carbon fibers are important in the area of composite materials. As a result, it is essential to understand the nature of chemical and physical processes at the interface. Numerous investigations in the area of interface characterization of polymer matrix composites have been reported (1-6).

Some of them were associated with chemical interactions of polymer matrices with modified carbon fibers (1-3). It is well known that surface treatment of carbon fibers is necessary to improve subsequent composite properties. This is because the treatment can increase surface functional groups as an aid to better fiber/matrix bonding. Infrared spectroscopy has shown surface oxygen present as carbonyl (C=O), ether (C-O-C), alcohol (C-OH), and carboxylic acid (COOH) (1, 2). Whang and Liu suggested that carboxylic acid and alcohol groups on the fiber surface reacted with carboxylic acid groups of the polyimide precursor during thermal treatment to form anhydride and ester groups, respectively (1). Scola et al. have shown increased room temperature shear strength as the oxygen concentration of carbon fiber surface was increased (2). Wei et al. grafted different monomers (maleic acid anhydride, norbornene acid anhydride) onto carbon fibers using a cold, low pressure plasma treatment (3). Increases in room temperature interlaminar shear strength (ILSS) (more than 100%) were observed as compared with untreated fibers.

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Several other investigations were related to molecular orientation of polymers adsorbed onto fiber surfaces (4-6). Nguyen and Ishida used reflection-absorption infrared (RAIR) spectroscopy to determine preferential orientation of adsorbed poly (aryl ether ether ketone) (PEEK) and model compounds with respect to the basal plane of a graphite single crystal (4). For model compounds such as 4(4-benzoylphenoxy)phenoxybenzene (BPPB) and 4,4'-diphenoxy-benzophenone (DPBP), significant differences were observed between transmission and RAIR spectra. Bands attributed to the carbonyl stretching mode and to the aromatic CH out-of-plane bending mode completely disappeared in the RAIR spectra of BPPB and DPBP adsorbed onto graphite substrtaes, respectively. It was thus concluded that BPPB and DPBP molecules were both adsorbed perpendicular to the graphite basal planes. The preferred orientation of the PEEK chains was also found to be perpendicular to the substrate when the polymer films were crystallized via annealing. However, the differences between the transmission and RAIR spectra of PEEK were not striking because of the semicrystalline nature of the polymer.

Very recently, scanning tunneling microscopy (STM) and near-edge X-ray absorption spectroscopy (NEXAFS) were used to obtain more information about the molecular orientation of a polyimide derived from pyromellitic dianhydride (PMDA) and oxydianiline (ODA) deposited onto a highly oriented pyrolytic graphite (HOPG) substrtae (5, 6). Sotobayashi et

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al. prepared a Langmuir-Blodgett (LB) film of a precursor consisting of a polyamic acid alkylamine salt which was then deposited onto the HOPG substrate (5). A monolayer film of PMDA/ODA polyimide was achieved by removal of the long alkyl chain during thermal or chemical treatments. Results obtained from STM showed that the pyromellitimide plane of the segement unit lay at a small angle of tilt relative to the HOPG surface (5). Results obtained from nitrogen near-edege X-ray absorption spectrum (NEXAFS) of a polyimide monolayer on HOPG also indicated that both the imide and phenyl rings lay nearly parallel to the graphite surface (6).

Polyimides derived from pyromellitic dianhydride (PMDA) and 2,2-bis[4-(4-aminophenoxy)-phenyl]-hexafluoropropane (4-BDAF) have potential applications as sizing agents for graphite fibers in advanced composites and as erosion-resistant coatings for composites. As a result, it is essential to determine the molecular structure of interfaces between PMDA/4-BDAF polyimides and graphite fibers. However, very little information has been obtained regarding the effect that substrates have on the molecular structure of this polyimide.

We have recently utilized various techniques such as surface-enhanced Raman scattering (SERS), RAIR, and x-ray photoelectron spectroscopy (XPS) to determine the molecular structure of the interface between PMDA/4-BDAF polyimides and silver and fiber substrates (7, 8). Results obtained

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suggested that imidization of polyamic acid films deposited onto silver substrates was inhibited by formation of silver carboxylates during curing. On the other hand, polyamic acid films were fully imidized at the HOPG surfaces. Thus, the thermal curing of polyamic acid for PMDA/4-BDAF polyimide at the substrate surfaces was strongly dependent on the nature of the substrates.

It is well known that RAIR spectroscopy is very sensitive to the preferential orientation of functional groups at the surface and that vibrational modes having transition moments normal to the surface appear with much greater intensity than do vibrations having transition moments parallel to the surface (9). In previous investigations, we used RAIR to determine the molecular orientations of polyimides and model compounds adsorbed onto the silver surfaces (7, 10, 11).

The primary purpose of this paper is to report results we have obtained using RAIR to determine molecular orientation of adsorbed PMDA/4-BDAF polyimides with respect to highly oriented pyrolytic graphite (HOPG) surfaces. HOPG was viewed as a model for graphite fibers. Pyromellitic diimide (PMDI), N,N'-diphenylpyromellitic diimide (DPPMDI), and PMDA/ODA polyimide, which were considered as model compounds for PMDA/4-BDAF polyimides, were also investigated (see Figure 1).

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II. Experimental

Pyromellitic diimide (PMDI) was obtained from Aldrich. N,N'-diphenylpyromellitic diimide (DPPMDI) was synthesized as follows. Pyromellitic dianhydride (PMDA, 99.0%) and aniline (99.5%) obtained from Aldrich were added into N-methylpyrrolidone (NMP) in a 2:1 mole ratio to make a 10% solution by weight. The solution was heated to 175°C under flowing N_2 for 1.5 hours during which time pale yellow particles precipitated. At the end of the reaction, the precipitate was washed with dimethylformamide (DMF) several times, recrystallized from a DMF-methanol mixed solvent, and dried under vacuum. The polyamic acid of PMDA and oxydianiline (ODA) was obtained from DuPont Corporation, while the polyamic acid of PMDA and 2,2-bis[4-(4-amino-phenoxy)-phenyl]-hexafluoropropane (4-BDAF) was obtained from Ethyl Corporation. Both the polyamic acids were supplied as solutions in NMP.

Samples were prepared for RAIR investigations as described below. Highly oriented pyrolytic graphite (HOPG) substrates (Union Carbide) were freshly cleaved, ultrasonically cleaned in acetone, and then blown dry with nitrogen. PMDI and DPPMDI films were deposited by placing a few drops of solutions in DMF onto the cleaned HOPG substrates and then dried under vacuum. The polyamic acid films of PMDA/ODA and PMDA/4-BDAF were deposited by placing a few drops of solutions in NMP onto the cleaned HOPG substrates and then cured at 107°C for 15 minutes and at

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$200^{\circ}C$ for an additional 15 minutes in an oven purged with argon.

RAIR spectra of organic films deposited on HOPG substrates were obtained using a Perkin-Elmer Model 1800 Fourier-transform infrared (FTIR) spectrophotometer and external reflection accessories provided by Harrick Scientific Co. One reflection at an angle of 78° was used in all cases. Spectra were collected in the quantitative mode at a resolution of 4 cm^{-1}. Sixty-four to 128 scans were averaged for each spectrum collected. The spectra reported are actually difference spectra obtained by subtracting spectra of baselines (substrates) from spectra of sample surfaces. Transmission infrared spectra were also obtained using the same spectrophotometer. Samples were prepared by mixing a small amount of powdered sample with potassium bromide powder and then pressing the mixture into a clear pellet under high pressure.

Similar techniques were used to determine the thickness of the organic films deposited on the HOPG substrates. The thickness of the films was measured using a Rudolph Research Model 436 ellipsometer to examine the substrates before and after deposition of the organic films. The light source was a mercury lamp (5461 angstroms in wavelength) with a green filter placed between the source and the polarizer. Angle of incidence was 60°.

III. Results and Discussion

A. Pyromellitic Diimide (PMDI). Transmission infrared spectrum of PMDI is shown in Figure 2 and the observed bands are summarized in Table I. Most of the observed bands were assigned to vibrations characteristic of the imide group (10, 12, 13). The remaining bands were assigned to vibrations of a 2,3,5,6-tetrasubstituted benzene derivative using the numbering system that was introduced by Wilson (14) and summarized by Varsanyi (15).

Reflection-absorption infrared (RAIR) spectra were obtained from PMDI films deposited onto highly oriented pyrolytic graphite (HOPG) substrates from 1%, 0.5%, and 0.05% solutions in dimethylformamide (DMF) (see Figure 3). The observed bands are also summarized in Table I. The RAIR spectrum obtained from films deposited onto HOPG from a 1% solution in DMF was similar to the transmission infrared spectrum of bulk PMDI (see Figures 2 and 3A). The prominent bands near 1779 and 1729 cm^{-1} were assigned to the "in-phase" and "out-of-phase" stretching modes of carbonyl groups (imide I). Medium intensity bands near 1379 and 1062 cm^{-1} were related to axial and transverse stretching modes of the CNC bond (imides II and III), respectively. The bands attributed to the CNC out-of-plane bending modes (imide IV) appeared near 766 and 729 cm^{-1}.

Other bands in the infrared spectra were related to the vibrations of the benzene ring. Medium intensitty bands near 1307 and 1156 cm^{-1} were assigned to $\nu(14)$, a ring

stretching mode, and to $\nu(13)$, a mode related to the stretching vibration between the rings and the substituents, respectively. Weak bands due to $\nu(19b)$ and $\nu(19a)$, ring stretching modes, were found near 1567 and 1470 cm^{-1}, respectively. Another band near 637 cm^{-1} was assigned to $\nu(12)$, a radial skeletal vibration.

As the thickness of the films was decreased, the bands near 766 and 729 cm^{-1} became considerably stronger relative to the bands near 1779 and 1729 cm^{-1}. When the RAIR spectrum of PMDI films deposited onto HOPG from the 0.05% solution was obtained (see Figure 3C), the bands near 1779 and 1729 cm^{-1} assigned to the carbonyl stretching modes, and those near 1379 and 1062 cm^{-1} assigned to the CNC axial and transverse stretching modes, almost disappeared. However, the bands near 766 and 729 cm^{-1} assigned to the CNC out-of-plane bending modes were strongly observed in the spectrum.

The results obtained from infrared spectroscopy indicated that the orientation of the molecules in adsorbed PMDI films depended on the film thickness. For relatively thick films, the spectra were dominated by absorption due to randomly oriented molecules and were similar to the bulk spectrum of PMDI. However, for thin films, the spectra were determined by the orientation of the molecules adjacent to the substrate.

As indicated above, RAIR spectroscopy is very sensitive to the preferential orientation of functional groups at the surface. Vibrational modes having transition moments normal

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to the surface appear with much greater intensity than do vibrations having transition moments parallel to the surface (9). For PMDI adsorbed flat-down with the imide rings parallel to the surface, the bands near 766 and 729 cm^{-1} were expected to be strong since they were assigned to the CNC out-of-plane bending modes and involved atomic motions that were mostly perpendicular to the surface. However, for PMDI adsorbed flat-down, the carbonyl stretching modes and the axial and transverse stretching modes of the CNC groups were mostly parallel to the surface and the corresponding bands should be weak. Thus, it was concluded that PMDI was adsorbed flat-down with the imide rings parallel to the HOPG surface. The orientation of adsorbed PMDI with respect to the HOPG surface was different from that with respect to the silver surface. As mentioned above, PMDI was adsorbed onto silver end-on with one imide group adjacent to the surface (10).

B. N,N'-Diphenylpyromellitic Diimide (DPPMDI). Transmission infrared spectrum of DPPMDI is shown in Figure 4 and the observed bands are also summarized in Table I. The spectrum was dominated by bands due to the characteristic vibrations of the imide groups (10, 12, 13). Other bands associated with the 2,3,5,6-tetrasubstituted and monosubstituted benzene rings were assigned using Wilson's numbering system (14, 15).

RAIR spectra were obtained from DPPMDI films deposited onto the HOPG substrates from 0.05%, 0.01%, and 0.005%

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solutions in hot DMF (see Figure 5). The observed bands are also summarized in Table I. RAIR spectra obtained from films deposited onto HOPG from 0.05% solutions in DMF were similar to transmission infrared spectra of the bulk DPPMDI (see Figures 4 and 5A). These spectra were characterized by bands near 1785 and 1722 cm^{-1}, which were assigned to the "in-phase" and "out-of-phase" stretching modes of carbonyl groups (imide I). A strong band near 1401 cm^{-1} assigned to the CNC axial stretching mode (imide II) was also observed in the spectra. Weak bands attributed to the CNC out-of-plane bending and transverse stretching modes (imide IV and III) were observed near 719 and 1129 cm^{-1}, respectively. Other bands observed in the spectra were assigned to the 2,3,5,6-tetrasubstituted and monosubstituted benzene rings. For example, a strong band near 1504 cm^{-1} was assigned to the tangential ring stretching mode $\nu(19a)-C_6H_5$. Weak bands attributed to the out-of-plane bending modes $\nu(17b)$, $\nu(10a)$, $\nu(11)$, and $\nu(4)$ of the monosubstituted benzene rings were observed near 869, 841, 742, and 686 cm^{-1}, respectively.

As the thickness of the films was decreased, the bands near 1785 and 1722 cm^{-1}, which were assigned to the stretching modes of carbonyl groups, became considerably stronger relative to the band near 1401 cm^{-1}, which was assigned to the axial stretching mode of the CNC bond (see Figures 5B-C). The band near 1129 cm^{-1} assigned to the CNC transverse stretching mode also increased its relative intensity. Moreover, the bands near 869, 841, 742, and 686

cm^{-1}, which were attributed to the out-of-plane bending modes of monosubstituted benzene rings, became considerably stronger relative to the band near 1401 cm^{-1}, which was assigned to the axial stretching mode of the CNC bond.

This is exactly the behavior expected if the molecules nearest to the HOPG surface were adsorbed edge-on with the carbonyl groups perpendicular to the surface and with the monosubstituted benzene rings parallel to the surface. In that case, the transition moments for the stretching modes of carbonyl groups and the transverse stretching mode of the CNC bond would be perpendicular to the surface, resulting in relatively high intensity for these modes. The transition moment for the axial stretching mode of the CNC bond would be parallel to the surface, resulting in relatively low intensity for this mode. Moreover, the transition moments for the out-of-plane bending modes of monosubstituted benzene rings would be perpendicular to the surface, resulting in relatively high intensity for these modes. Thus, it was concluded that DPPMDI was adsorbed edge-on with two carbonyl groups adjacent to the HOPG surface and with the monosubstituted benzene rings parallel to the HOPG surface. The orientation proposed here was similar to that for DPPMDI adsorbed onto the silver surface (10).

C. PMDA/ODA Polyimides. Transmission infrared spectra of the polyamic acid of PMDA/ODA before and after curing are shown in Figure 6 and the observed bands are summarized in Tables II and III, respectively. Bands near 1717, 1303, and

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1407 cm^{-1} in the infrared spectrum of the polyamic acid before curing (see Figure 6A) were assigned to the C=O stretching, C-O stretching, and COH in-plane bending (11, 16) modes of the acid groups, respectively. Bands near 1670 and 1545 cm^{-1} were assigned to vibrational modes of amide groups (17). The strong, sharp band near 1499 cm^{-1} was assigned to the tangential ring stretching mode $\nu(19a)$-C$_6$H$_4$ of the di-substituted rings while the strong, broad band near 1237 cm^{-1} was assigned to a stretching mode of the COC groups in the ODA moieties.

Bands near 1717, 1670, 1545, 1407, and 1303 cm^{-1} which were characteristic of amide and acid groups all disappeared after curing (see Figure 6B) while bands characteristic of imide groups appeared near 1777, 1725, 1378, and 1116 cm^{-1} (10-13). The bands near 1777 and 1725 cm^{-1} were assigned to in-phase and out-of-phase C=O stretching modes of the imide groups, respectively. Those near 1378 and 1116 cm^{-1} were attributed to the axial and transverse CNC stretching modes of the imide groups.

RAIR was also used to investigate the curing of thin polyamic acid films of PMDA/ODA deposited onto the HOPG substrates. RAIR spectra obtained before and after curing of thin polyamic acid films deposited onto HOPG from 1%, 0.2%, and 0.04% solutions in N-methyl pyrrolidone (NMP) were shown in Figures 7 and 8, respectively. The observed bands are also summarized in Tables II and III. Generally speaking, the RAIR spectra of polyamic acid films adsorbed

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onto HOPG substrates before curing (see Figure 7) were similar to the transmission infrared spectra of the polyamic acid (see Figure 6A). However, the RAIR spectra of these films adsorbed onto the HOPG substrates and then cured in an argon-purged oven at 107°C for 15 minutes and at 200°C for an additional 15 minutes (see Figure 8) were significantly different from the transmission spectra of the bulk polyimide (see Figure 6B). For example, the bands near 1499, 1378, and 1237 cm^{-1} were much weaker than the band near 1725 cm^{-1} in the RAIR spectra even though they had nearly the same intensity in the transmission infrared spectrum. No bands associated with new chemical species were observed in the RAIR spectra, indicating that the differences in relative intensities between the RAIR and transmission infrared spectra of the polyimide were related to orientation effects.

For PMDA adsorbed with the edge-on orientation, the band near 1725 cm^{-1} was expected to increase in intensity relative to the band near 1378 cm^{-1} as the thickness of the PMDA/ODA films decreased since in that case the transition moment for the C=O stretching mode would be perpendicular to the surface and that for the axial CNC stretching mode would be parallel. The bands near 1499 and 1237 cm^{-1}, which were assigned to the tangential ring stretching and COC stretching modes of the ODA moieties, were always relatively weak, implying that the ODA moieties were mostly parallel to the surface. Thus, it was concluded that the PMDA moieties

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were oriented edge-on with the C=O groups perpendicular to the HOPG surface and that the ODA moieties were oriented mostly parallel to the HOPG surface.

Considering that the relative intensities of the bands near 1499, 1378, and 1237 cm^{-1} did not change much relative to that near 1725 cm^{-1} as the film thickness decreased (see Figure 8), it was concluded that the preferential orientation of the polyimide molecules on the HOPG surface extended into the bulk of the polyimide at least several molecular layers. The orientation of the PMDA and ODA moieties with respect to the HOPG surface that is proposed here would require the plane of the rings in the ODA moieties to be inclined with respect to the plane of the PMDA rings. In fact, such a model has been proposed by Silverman et al., who suggested that the angle between the PMDA and ODA rings was 60° (18). We have reported a similar orientation when RAIR was used to determine the molecular structure of the interface formed by chemically curing the polyamic acid of PMDA/ODA against silver substrates (11).

The orientation proposed here is apparently different from that reported by Sotobayashi et al. (5, 6). The reason for observing this phenomenon is not clear but could be due to different preparations of samples.

D. PMDA/4-BDAF Polyimides. Transmission infrared spectra of the polyamic acid of PMDA/4-BDAF before and after curing are shown in Figure 9 and the observed bands are summarized in Tables II and III, respectively. The spectrum of the

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polyamic acid before curing was characterized by strong bands near 1724, 1667, 1610, 1503, 1246, 1205, and 1175 cm^{-1} and by weaker bands near 1779, 1545, and 1408 cm^{-1} (see Figure 9A). The strong band near 1724 cm^{-1} was assigned to the C=O stretching mode of acid groups (11, 16). The strong, broad band near 1667 cm^{-1} and the weak band near 1545 cm^{-1} were attributed to the amide I and II modes (16, 17). A strong band near 1503 cm^{-1} was assigned to the tangential ring stretching mode ν(19a) of the C_6H_4 rings while another strong band near 1175 cm^{-1} was assigned to the C-X stretching mode ν(13) of the C_6H_2 rings. Strong bands near 1246 and 1205 cm^{-1} were assigned to the COC asymmetric stretching and symmetric CF_3 stretching modes of the 4-BDAF moieties, respectively.

When the polyamic acid was cured (see Figure 9B), the bands near 1667, 1545, and 1408 cm^{-1} due to the amide groups disappeared and new bands near 1779, 1728, 1379, and 1116 cm^{-1} due to the imide groups appeared. The bands near 1779 and 1728 cm^{-1} were assigned to C=O stretching modes of the imide groups, while those near 1379 and 1116 cm^{-1} were assigned to the axial and transverse CNC stretching modes of the imide groups.

RAIR was also utilized to investigate the curing of thin polyamic acid films deposited onto the HOPG substrates. RAIR spectra were obtained before and after curing of thin polyamic acid films deposited onto HOPG substrates from 1%, 0.25%, and 0.05% solutions in NMP (see Figures 10 and 11).

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Generally speaking, RAIR spectra of these films adsorbed onto the HOPG substrates before and after curing (see Figures 10 and 11) were similar to transmission spectra of the bulk polyamic acid and polyimide, respectively (see Figures 9A and 9B).

The orientation of PMDA/ODA polyimide with respect to the HOPG surface was apparently different from that of PMDA/4-BDAF polyimide on the HOPG surface. The RAIR spectra obtained from these films after curing were similar to the transmission spectra of the bulk polyimide, implying that the PMDA/4-BDAF polyimide was randomly oriented on the HOPG surface. The reason for observing this phenomenon is not understood yet but could be due to different crystallinities of polymer chains. Nguyen and Ishida have shown that the crystallinity of the polymer chains could significantly affect the surface-induced orientation (4). Preferential orientation with respect to the basal plane of graphite single crystals was not observed for randomly oriented PEEK. However, the preferred orientation was found to be perpendicular to the surface for the crystalline PEEK.

The case of HOPG substrates was also different from that of silver substrates. Results obtained from SERS, RAIR, and XPS have shown that imidization was inhibited by formation of carboxylates at the polyamic acid/silver interface upon curing (7, 8). Thus, the thermal curing of polyamic acid for PMDA/4-BDAF polyimide at the substrate

surfaces was strongly dependent on the nature of the substrates.

IV. Conclusions

Characterization of interfaces between polyimides and carbon fibers is important in the area of composite materials. It is known that reflection-absorption infrared (RAIR) spectroscopy is very sensitive to the preferential orientation of functional groups at the surface and that vibrational modes having transition moments normal to the surface appear with much greater intensity than do vibrations having transition moments parallel to the surface. As a result, RAIR was used to determine the orientations of adsorbed polyimides and model compounds with respect to highly oriented pyrolytic graphite (HOPG) surfaces. Among the model compounds, pyromellitic diimide (PMDI) was adsorbed flat-down with the imide rings parallel to the surface, while N,N-diphenyl PMDI (DPPMDI) was adsorbed edge-on with the carbonyl groups perpendicular to the surface and with the monosubstituted benzene rings parallel to the surface.

For polyimides derived from pyromellitic dianhydride (PMDA) and oxydianiline (ODA), the PMDA moieties were oriented edge-on with the carbonyl groups perpendicular to the surface and the ODA moieties oriented mostly parallel to the surface. However, polyimides derived from PMDA and 2,2-bis[4-(4-aminophenoxy)-phenyl]-hexafluoro-propane (4-BDAF), were randomly oriented on the HOPG surface. The differences

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in orientation observed between PMDA/ODA and PMDA/4-BDAF polyimides adsorbed onto HOPG surfaces could be due to different crystallinities of polymer chains. It was also found that the thermal curing of polyamic acid for PMDA/4-BDAF polyimide at the substrate surfaces was strongly dependent on the nature of the substrates.

V. Acknowledgements

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Table I. Tentative band assignments for pyromellitic diimide (PMDI) and N, N-diphenyl pyromellitic diimide (DPPMDI).

| (PMDI) | | (DPPMDI) | | |
IR	RAIR (cm^{-1})	IR	RAIR	Assignment
1772(S)	1779(W)	1786(W)	1785(M)	ν(C=O), in-phase
1720(S)	1729(W)	1724(S) 1710(S)	1722(S)	ν(C=O), out-of-phase }imide I
		1599(W)	1600(W)	ν(8a)-C_6H_5
		1503(M)	1504(W)	ν(19a)-C_6H_5
1567(W)		1453(W)		ν(19b)-C_6H_2
1470(W)	1471(W)			ν(19a)-C_6H_2
1379(M)	1383(W)	1399(S)	1401(W)	ν(CNC),axial,imide II
1307(M)	1311(W)			ν(14)-C_6H_2
		1290(W)		ν(3)-C_6H_5
1156(W)	1156(W)			ν(13)-C_6H_2
1062(M)	1062(W)	1130(M)	1129(M)	ν(CNC), transverse, imide III
		1024(W)		ν(18b)-C_6H_5
		918(W)		ν(17a)-C_6H_5
		868(W)	869(M)	ν(17b)-C_6H_5
		843(M)	841(M)	ν(10a)-C_6H_5
		742(S)	742(M)	ν(11)-C_6H_5
775(W)	766(S)			} CNC out-of-plane
728(M)	729(S)	721(S)	719(W)	bending, imide IV
		687(M)	686(M)	ν(4)-C_6H_5
637(W)	638(W)			ν(12)-C_6H_2

(S) = strong; (M) = medium; (W) = weak

Table II. Tentative band assignments for polyamic acids of
PMDA/ODA and PMDA/4-BDAF polyimides.

(PMDA/ODA)		(PMDA/4-BDAF)		
IR	RAIR (cm^{-1})	IR	RAIR	Assignment
1720(M)	1720(M)	1724(M)	1723(M)	ν(C=O), acid
1670(S)	1670(S)	1667(M)	1663(M)	ν(C=O), amide I
1610(W)	1609(W)	1610(M)	1608(M)	ν(8a)
1545(M)	1542(M)	1545(M)	1542(M)	β(CNH), amide II
1499(S)	1500(S)	1503(S)	1502(S)	ν(19a)-C_6H_4
1407(M)	1409(M)	1408(M)	1410(W)	ν(CN), amide III
1303(M)	1304(M)	1301(W)	1301(W)	ν(COH), acid
1237(M)	1240(M)			ν_a(COC)
		1246(S)	1248(S)	ν_a(COC) + ν_a(CF$_3$)
		1205(M)	1206(M)	ν_s(CF$_3$)
1170(W)	1170(W)	1174(S)	1172(S)	ν(13)-C_6H_2
1014(W)	1015(W)	1016(W)	1017(W)	ν(18a)-C_6H_4

(S) = strong; (M) = medium; (W) = weak
s = symmetric; a = asymmetric

Table III. Tentative band assignments for PMDA/ODA and
PMDA/4-BDAF polyimides.

(PMDA/ODA)		(PMDA/4-BDAF)		
IR	RAIR (cm^{-1})	IR	RAIR	Assignment
1777(M)	1778(W)	1779(W)	1780(W)	ν(C=O), in-phase
1725(S)	1730(S)	1728(S)	1730(S)	ν(C=O), out-of-phase }imide I
1605(W)	1609(W)			ν(8a)-C_6H_2
		1600(W)	1600(W)	ν(8a)-C_6H_4
1499(S)	1500(M)	1504(S)	1502(S)	ν(19a)-C_6H_4
		1456(W)		ν(19b)-C_6H_2
1378(S)	1379(W)	1379(S)	1380(S)	ν(CNC), axial, imide II
1239(S)	1240(W)			ν_a(COC)
		1248(S)	1250(S)	ν_a(COC)+ν_a(CF_3)
		1207(M)	1209(M)	ν_s(CF_3)
1169(M)	1169(W)	1176(M)	1178(M)	ν(13)-C_6H_2
1116(M)	1116(M)	1116(M)	1116(M)	ν(CNC), transverse, imide III
		1093(W)	1095(W)	ν(13)-C_6H_2
1015(w)		1017(W)		ν(18a)-C_6H_2

(S) = strong; (M) = medium; (W) = weak
s = symmetric; a = asymmetric
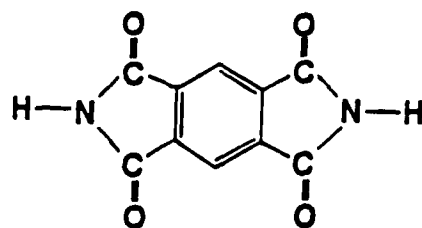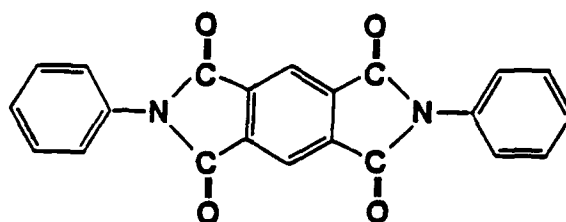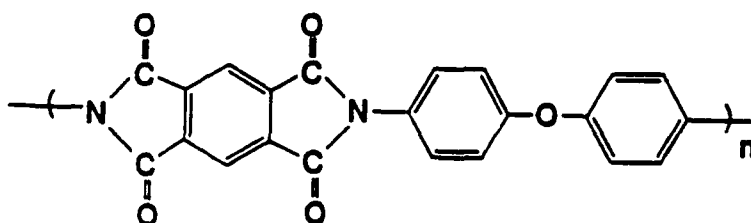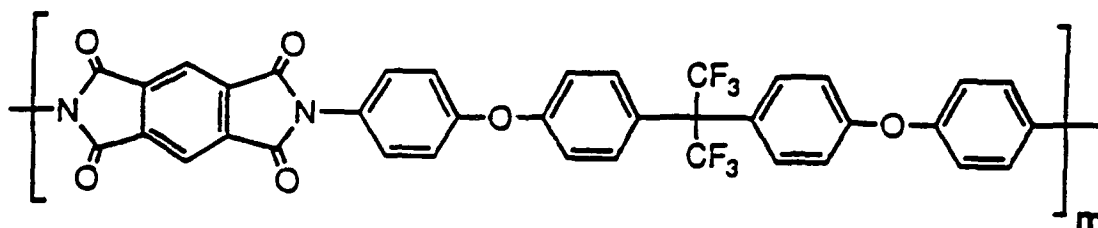
Figure 1. Molecular structures of (A) - pyromellitic diimide
(PMDI), (B) - N,N-diphenyl pyromellitic diimide (DPPMDI),
(C) - PMDA/ODA, and (D) PMDA/4-BDAF polyimides.
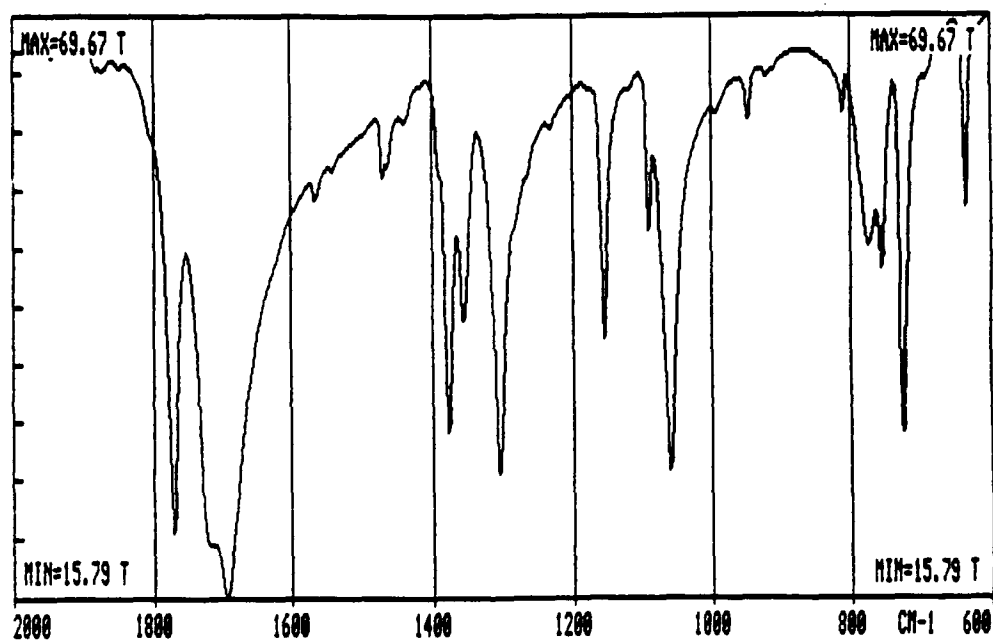
Figure 2. Transmission infrared spectrum of PMDI.
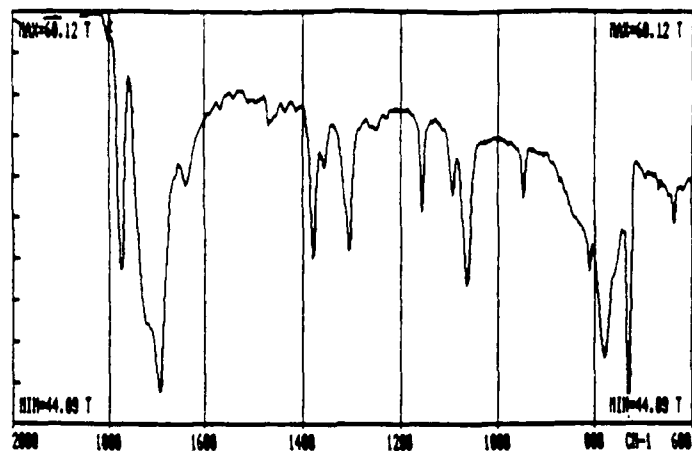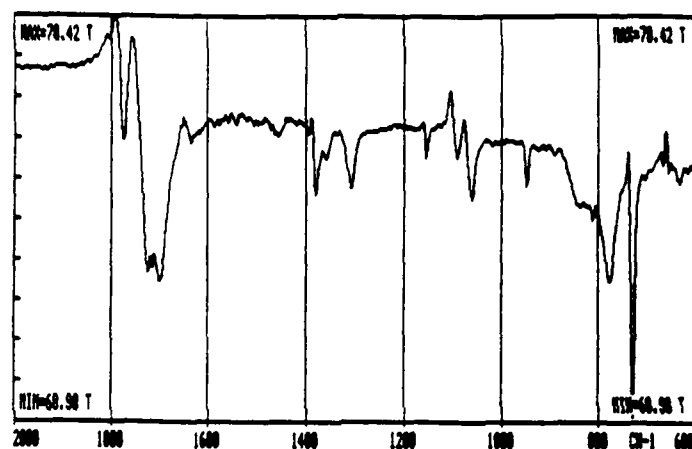
Figure 3. RAIR spectra obtained from thin PMDI films deposited onto HOPG substrates from (A) - 1%, (B) - 0.5%, and (C) - 0.05% solutions in DMF. The thicknesses were approximately 1420, 460, and 70 angstroms, respectively.
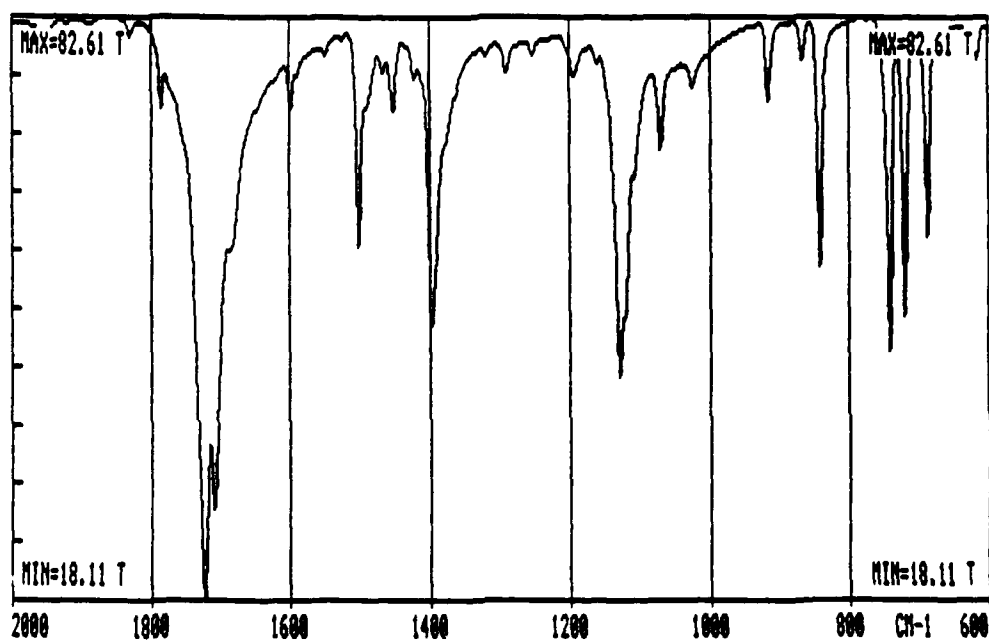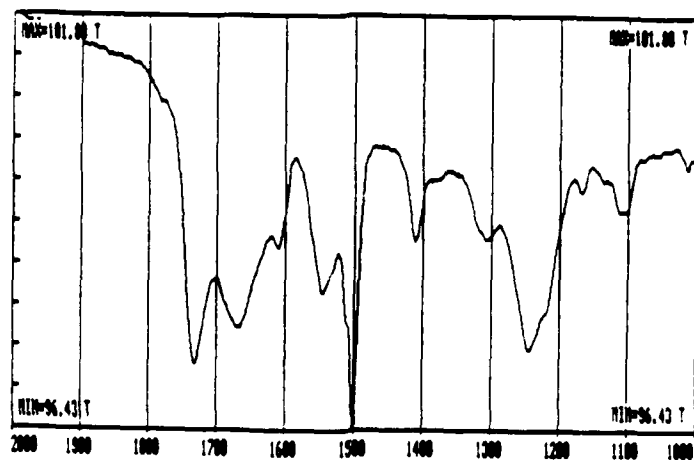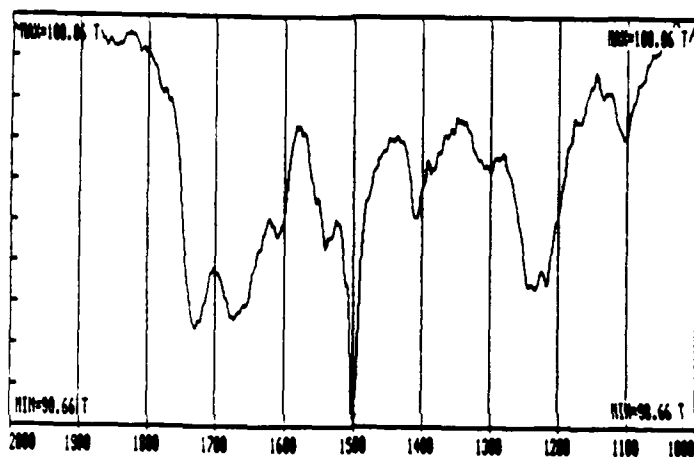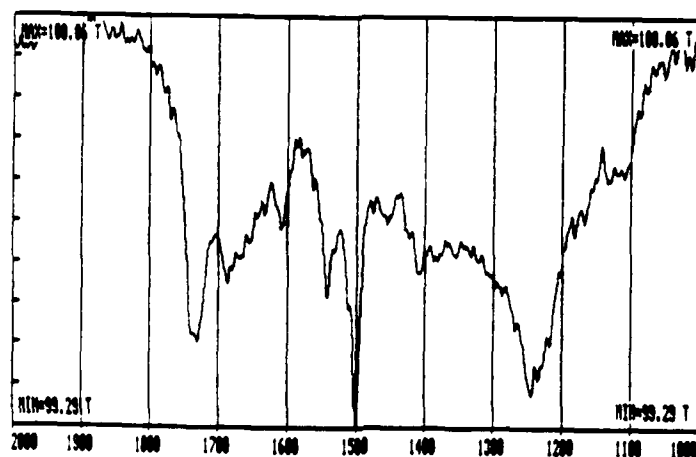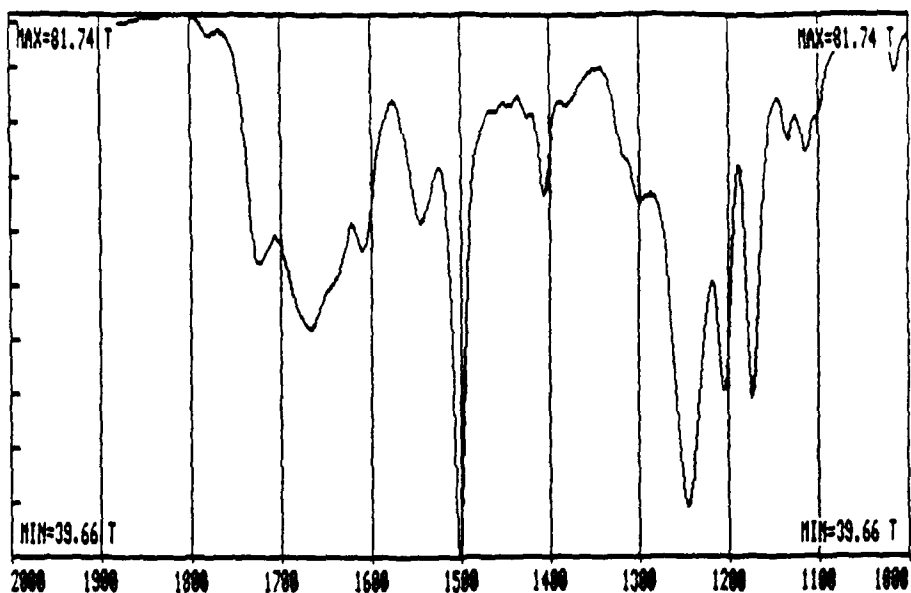
Figure 4. Transmission infrared spectrum of DPPMDI.
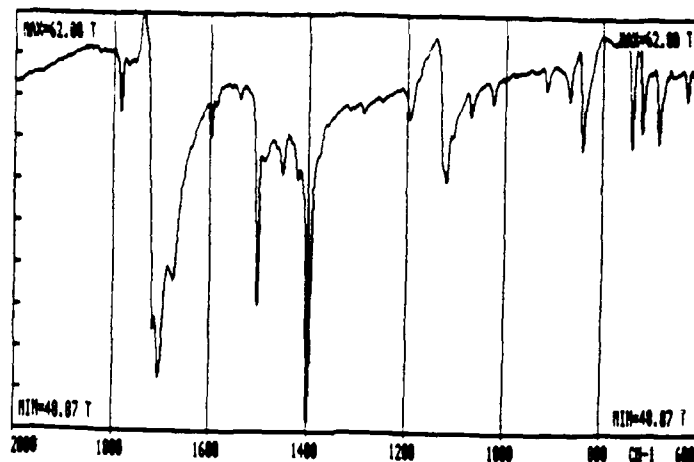
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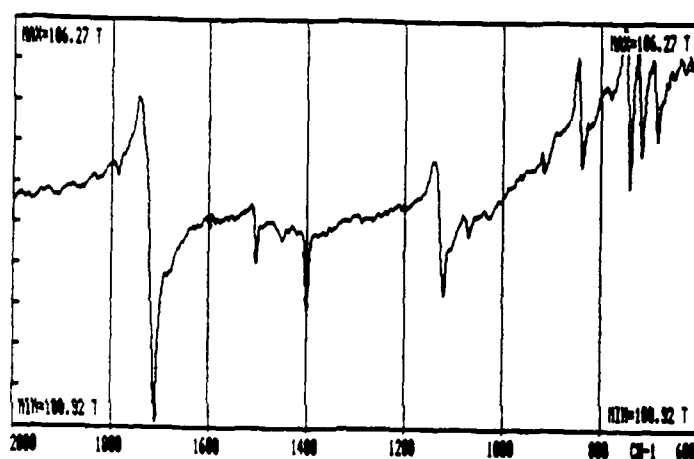
(B)
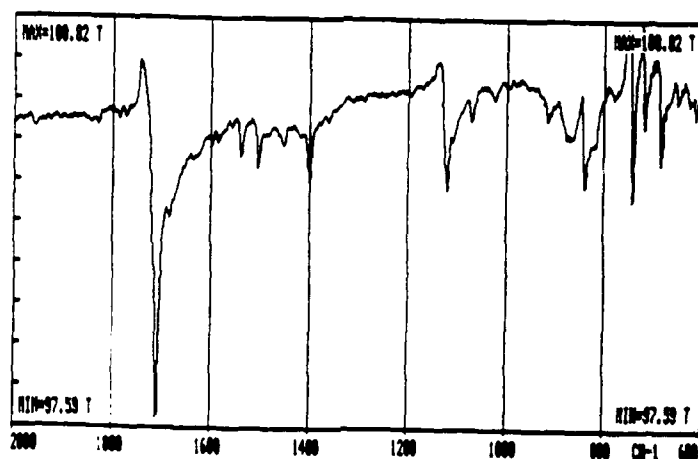
(C)

Figure 5. RAIR spectra of thin DPPMDI films deposited onto HOPG substrates from (A) - 0.05%, (B) - 0.01%, and (C) - 0.005% solutions in hot DMF. The thicknesses were approximately 1260, 360, and 50 angstroms, respectively.
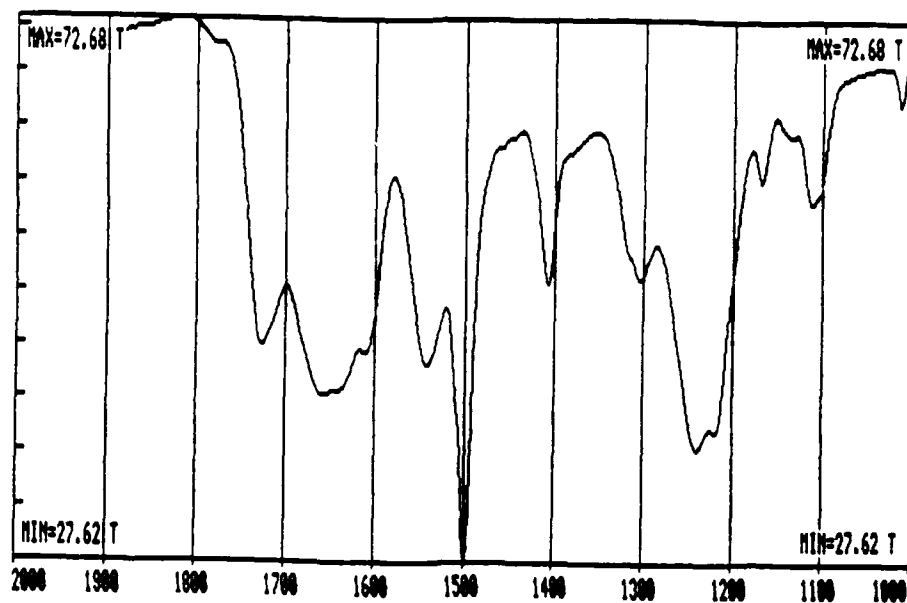
(A)
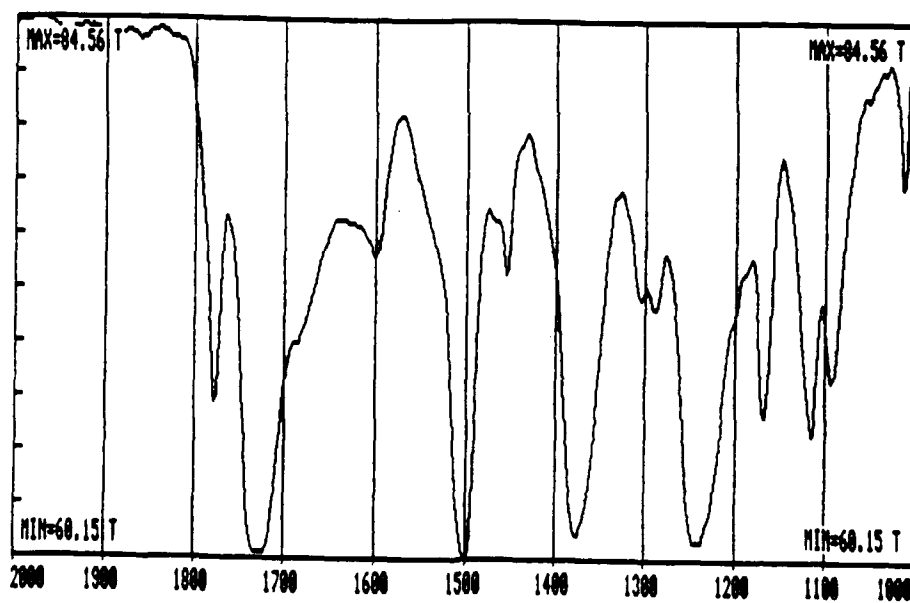
(B)

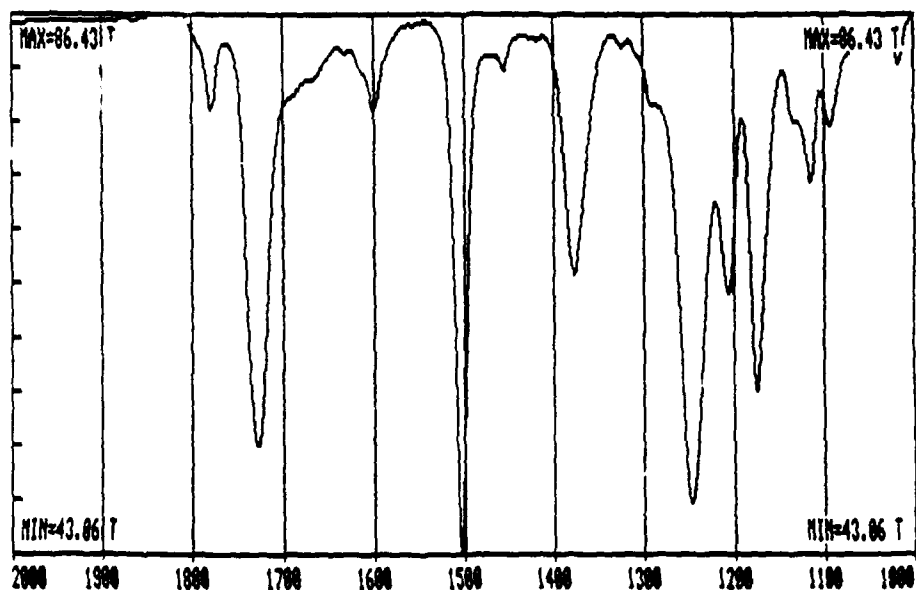Figure 6. Transmission infrared spectra of the polyamic acid
of PMDA/ODA (A) - before and (B) - after curing.

Figure 7. RAIR spectra obtained from thin films of the polyamic acid of PMDA/ODA deposited onto HOPG substrates from (A) - 1%, (B) - 0.2%, and (C) - 0.04% solutions in NMP before curing. The thicknesses were approximately 380, 120, and 30 angstroms, respectively.
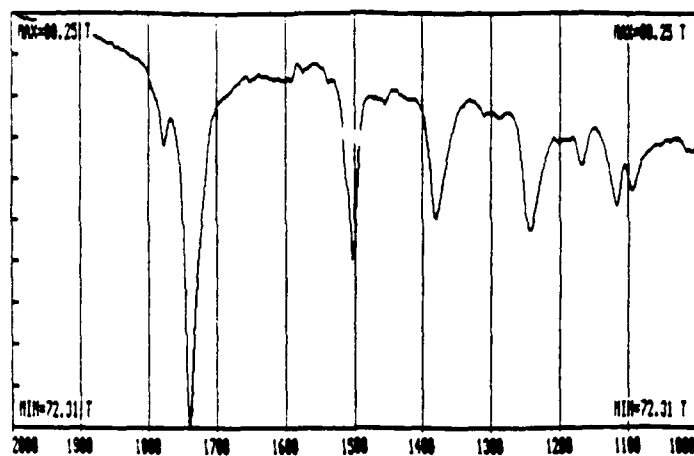
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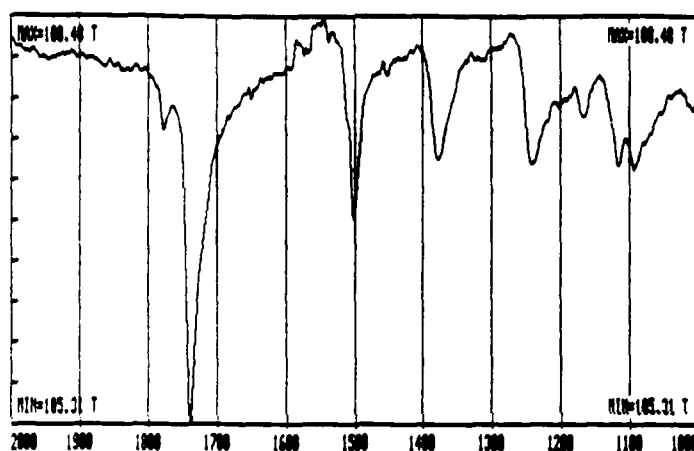
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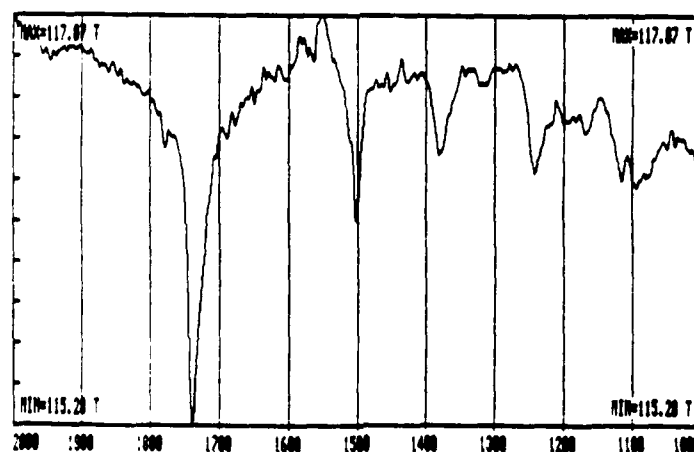
(C)

Figure 8. RAIR spectra obtained from thin films of the polyamic acid of PMDA/ODA deposited onto HOPG substrates from (A) - 1%, (B) - 0.2%, and (C) - 0.04% solutions in NMP and then curd at 107°C for 15 minutes and at 200°C for an additional 15 minutes in an oven purged with argon.
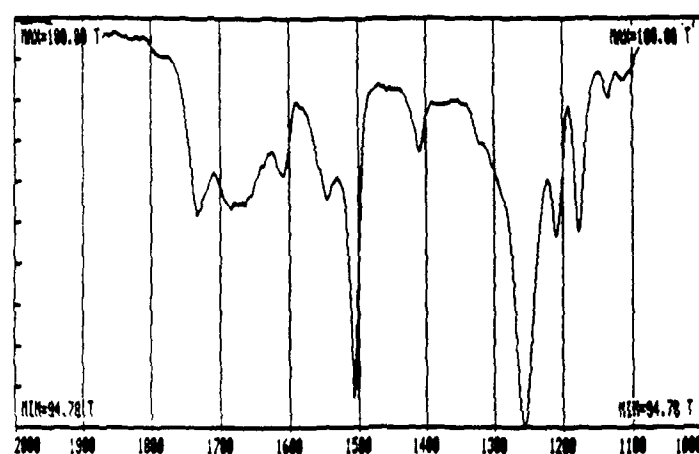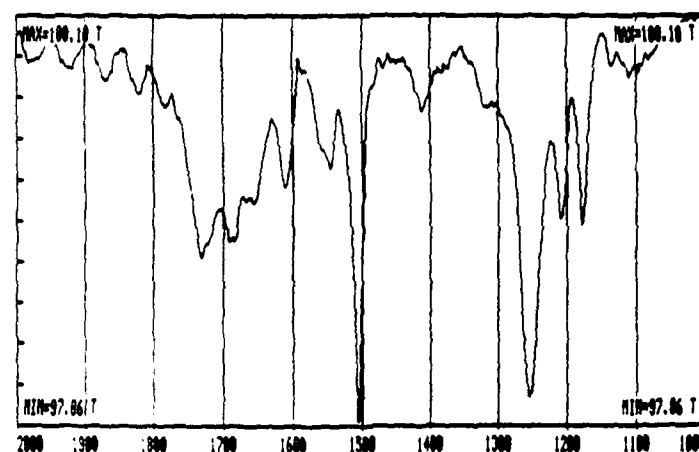
30

(A)

(B)

Figure 9. Transmission infrared spectra of the polyamic acid
of PMDA/4-BDAF (A) - before and (B) - after curing.
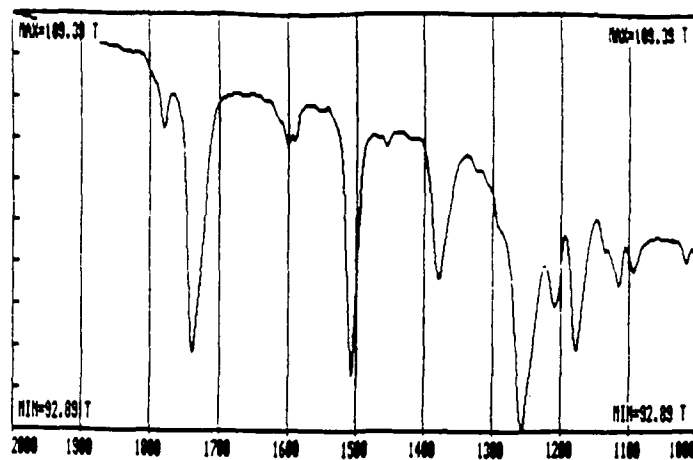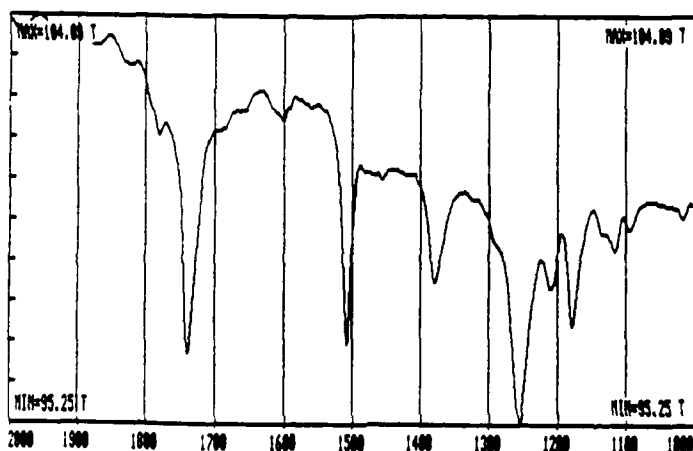
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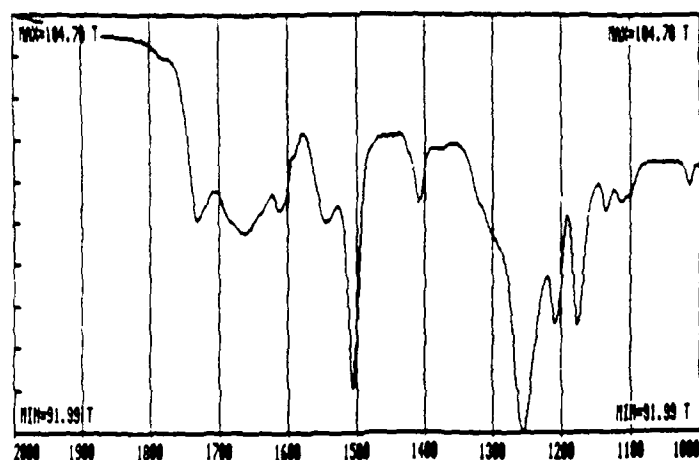
(A)

(B)

(C)

Figure 10. RAIR spectra obtained from thin films of the polyamic acid of PMDA/4-BDAF deposited onto HOPG substrates from (A) - 1%, (B) - 0.25%, and (C) - 0.05% solutions in NMP before curing. The thicknesses were approximately 1200, 420, and 60 angstroms, respectively.
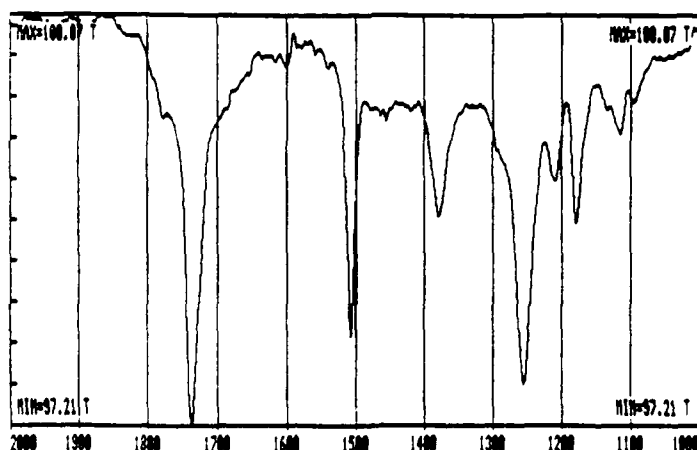
(A)

(B)

(C)

Figure 11. RAIR spectra obtained from thin films of the
polyamic acid of PMDA/4-BDAF deposited onto HOPG substrates
from (A) - 1%, (B) - 0.25%, and (C) - 0.05% solutions in NMP
and then cured at 107°C for 15 minutes and at 200°C for an
additional 15 minutes in an oven purged with argon.

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